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(54) BROMOALKYL BROMOALKANOATES, THEIR MANUFACTURE AND USE AS FLAMEPROOFING AGENTS

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides bromine compounds of the general formula

$$(1)\quad Y{-}(CH_2)_{m-1}{-}(CHBr)_r{-}(CH_2)_{n-1}{-}COO{-}(X_1{-}OOC)_{t-1}{-}(CH_2)_{p-1}{-}(CHBr)_s{-}(CH_2)_{q-1}{-}Y'$$

containing up to 14 bromine atoms, in which X_1 denotes alkylene or alkenylene with 2 to 6 carbon atoms which are optionally substituted by bromine or hydroxyl, each of Y and Y' independently denotes hydroxyl or hydrogen, each of *m, n, p* and *q* independently denote an integer from 1 to 13, at least two of the indices *m, n, p* and *q* being at least 2, each of *r* and *s* independently denotes an integer from 1 to 7, *t* denotes 1 or 2, with the proviso that the sum of $m + n + r$ is an integer from 4 to 20, the sum of $p + s + q$ is an integer from 4 to 20 and the sum of $m + n + p + q + r + s$ is an integer from 13 to 40, preferably 13 to 24.

The bromine compounds according to the invention are aliphatic brominated monoesters, if t in formula (1) is 1, and aliphatic brominated diesters, if t in formula (1) is 2.

If t in formula (1) is 1, $-(CH_2)_{m-1}-(CHBr)_r-(CH_2)_{n-1}-$ (referred to hereinafter as X') is derived from an aliphatic, saturated or ethylenically unsaturated monocarboxylic or ω—hydroxymonocarboxylic acid, whilst $-(CH_2)_{p-1}-(CHBr)_s-(CH_2)_{q-1}-$ (referred to hereinafter as X") is derived from an aliphatic, saturated or ethylenically unsaturated monoalcohol or α, ω—diol.

If t in formula (1) is 2, X' and X" are derived from an aliphatic, saturated or ethylenically unsaturated monocarboxylic or ω—hydroxymonocarboxylic acid, whilst X_1 is derived from an aliphatic, saturated or ethylenically unsaturated diol or polyol.

The groups X_1, X' and X" in formula (1) may be identical to or different from one another.

The bromine compounds of the formula (1) contain 2 to 14 bromine atoms. Compounds of the formula (1) which have 2 bromine atoms contain X' and X" radicals which are each substituted by 1 bromine atom and compounds of the formula (1) which have 14 bromine atoms contain X' and X" radicals which are each substituted by 1 to 7 bromine atoms and, where appropriate, a X_1 radical which is substituted by 2 to 12 bromine atoms.

When t = 2, the X' and X" radicals may suitably be derived, *inter alia*, from the following acids in brominated form: acetic acid, propionic acid, valeric acid, oenanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid or palmitic acid and, above all, from stearic acid and, in particular, butyric acid or caproic acid. Examples of a brominated aliphatic monocarboxylic acid which may be mentioned are 10, 11-dibromoundecanoic acid and, in particular, 2, 3, 4, 5-tetrabromocarproic acid.

Furthermore, the X' and X" radicals may suitably be derived, *inter alia*, from the following acids brominated at their double bonds:

acrylic acid, vinylacetic acid, caproleic acid, lauroleic acid, myristoleic acid, physetoleic acid and elaeostearic acid and, above all from crotonic acid, oleic acid, elaidic acid and, in particular, undecenoic acid or sorbic acid. Particularly preferred examples are brominated elaeostearic acid and sorbic acid.

Moreover, the X′ and X″ radicals may suitably be derived, *inter alia*, from glycollic acid, or β–hydroxypropionic acid in brominated form.

When t = 1, the X″ radicals may suitably be derived *inter alia*, from the following alcohols in brominated form: ethanol, butyl alcohol, amyl alcohol, hexanol, heptanol, n-octyl alcohol, nonyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol and cetyl alcohol and, in particular, from propyl alcohol, undecyl alcohol or stearyl alcohol. Particular examples are 10, 11-dibromoundecyl alcohol, 9, 10-dibromostearyl alcohol and, in particular, 2, 3-dibromopropyl alcohol.

Furthermore, the X″ radical may suitably be derived, *inter alia*, from the following alcohols brominated at their double bonds: vinyl alcohol, 2-butene-1, 4-diol, and, above all, allyl alcohol, 10-undecen-1-ol and oleyl alcohol.

Additionally, the X″ radical may suitably be derived, *inter alia*, from the following alcohols in brominated form: pentane-1, 5-diol, hexane-1, 6-diol and, above all, butane-1, 4-diol and, in particular ethylene glycol, an example being 2, 3-dibromobutane-1, 4-diol.

The X_1 radical may suitably be derived, *inter alia*, from propane-1, 2-diol, butane-2, 3-diol, pentane-1, 5-diol, neopentyl-glycol, dimethylolpropane, pinacone, hexane-1, 6- and -2, 5-diol, and, above all, from butane-1, 4-diol and, in particular, ethylene glycol. They can also be derived from brominated saturated diols, such as, for example, 3, 4-dibromobutane-1, 2-diol, and, in particular, 2, 3-dibromobutane-1, 4-diol or bis-(bromomethyl)-propane-1, 4-diol.

Furthermore, the X_1 radical may suitably be derived, *inter alia*, from 2-butene-1, 4-diol. 2, 3-Dibromo-2-butene-1, 4-diol may be mentioned as an example of an ethylenically unsaturated, brominated diol.

Finally, the X_1 radicals may suitably be derived, *inter alia*, from glycerol, sorbitol, mannitol or pentaerythritol.

Particluar brominated aliphatic monoesters or diesters of the present invention are of the formula

$$(2)\ H{-}(CH_2)_{m-1}{-}(CHBr)_r{-}(CH_2)_{n-1}{-}COO{-}(X_1{-}OOC)_{t-1}{-}(CH_2)_{p-1}{-}(CHBr)_s{-}(CH_2)_{q-1}{-}H$$

wherein X_1, m, n, p, q, r, s and t are as hereinbefore defined and, in particular, of the formula

$$(3)\ H{-}(CH_2)_{m'-1}{-}(CHBr)_{r'}{-}(CH_2)_{n'-1}{-}COO{-}(X_2{-}OOC)_{t-1}{-}(CH_2)_{p'-1}{-}(CHBr)_{s'}{-}(CH_2)_{q'-1}{-}H$$

wherein X_2 denotes alkylene with 2 to 4 carbon atoms which is optionally substituted by bromine or hydroxyl or denotes alkenylene with 2 to 4 carbon atoms which is optionally substituted by bromine, each of m', n', p' and q' independently denotes an integer from 1 to 10, two or three of the indices m', n', p' and q' being an integer from 2 to 10, each of r' and s' independently denotes an integer from 2 to 4 and t denotes 1 or 2, with the proviso that the sum of $m' + n' + r'$ is an integer from 4 to 20, the sum of $p' + s' + q'$ is an integer from 4 to 20, and the sum of $r' + s' + m' + n' + p' + q'$ is an integer from 13 to 40, preferably 13 to 24.

Amongst the bromine compounds according to the invention, the aliphatic monoesters are preferred to the aliphatic diesters.

Bromine compounds of thus further preferred type are aliphatic monoesters which correspond to the formula

$$(4)\ H{-}(CH_2)_{m''-1}{-}(CHBr)_{r'}{-}(CH_2)_{n''-1}{-}COO{-}(CH_2)_{p''-1}{-}(CHBr)_{s'}{-}(CH_2)_{q''-1}{-}H$$

wherein each of m'', n'', p'' and q'' independently denotes an integer from 1 to 9, two of the indices m'', n'', p'' and q'' being an integer from 2 to 9, each of r' and s' independently denotes an integer from 2 to 4, with the proviso that the sum of $m'' + n'' + r'$ is an integer from 4 to 20, the sum of $p'' + s' + q''$ is an integer from 4 to 20, and the sum of $r' + s' + m'' + n'' + p'' + q''$ is an integer from 13 to 40, preferably 13 to 24.

Valuable compounds are, above all, the aliphatic brominated monoesters or diesters which have a molecular weight of 300 to 1,300, preferably 440 to 900, and a bromine content of 30 to 80, e.g. 38 to 80, preferably 40 to 65, percent by weight.

Examples of bromine compounds according to the invention are:

(6.1) $CH_2Br{-}CHBr{-}(CH_2)_8{-}COO{-}CH_2{-}CHBr{-}CH_2Br$

(6.2) $CH_3{-}(CH_2)_7{-}(CHBr)_2{-}(CH_2)_7{-}COO{-}CH_2{-}CHBr{-}CH_2Br$

(6.3) $CH_3{-}(CHBr)_4{-}COO{-}(CH_2)_9{-}CHBr{-}CH_2Br$

(6.4) $CH_3{-}(CHBr)_2{-}COO{-}(CH_2)_9{-}CHBr{-}CH_2Br$

(6.5) $CH_3{-}(CHBr)_2{-}COO{-}(CH_2)_8{-}(CHBr)_2{-}(CH_2)_7{-}CH_3$

(6.6) $CH_2Br{-}CHBr{-}(CH_2)_8{-}COO{-}CH_2{-}CBr{=}CBr{-}CH_2{-}OOC{-}(CH_2)_8{-}CHBr{-}CH_2Br$

(6.7) $CH_2Br{-}CHBr{-}(CH_2)_8{-}COO{-}CH_2{-}(CHBr)_2{-}CH_2{-}OOC{-}(CH_2)_8{-}CHBr{-}CH_2Br$

(6.8) $CH_2Br-CHBr-(CH_2)_8-COO-CH_2-(CHBr)_2-CH_2-OH$

(6.9) $CH_3-(CHBr)_4-COO-(CH_2)_2-OOC-(CHBr)_4-CH_3$

(6.10) $CH_2Br-CHBr-(CH_2)_8-COO-(CH_2)_2-OOC-(CH_2)_8-CHBr-CH_2Br$

Amongst these, the compounds of the formula (6.1) are particularly valuable representatives of the monoesters.

The brominated monoesters are suitably manufactured as follows: an acid of the formula

(7) $Y-(CH_2)_{m-1}-Q-(CH_2)_{n-1}-COOH$

or its ester, anhydride or halide, especially chloride, is esterified or transesterified with an alcohol of the formula

(8) $HO-(CH_2)_{p-1}-Q'-(CH_2)_{q-1}-Y'$

in which formulae Y, Y', *m*, *n*, *p* and *q* are as hereinbefore defined and each of Q and Q' independently denotes alkylene, alkenylene or alkynylene with at most 7 carbon atoms, which are optionally substituted by 1 to 7 bromine atoms, the radicals Q and Q' being substituted by bromine and/or having a double or triple bond; and bromine or hydrogen bromide is added on at any double bonds or triple bonds which are present.

The brominated diesters are suitably manufactured as follows: an acid of the formula

(9) $Y-(CH_2)_{m-1}-Q-(CH_2)_{n-1}-COOH$

or its ester, anhydride or halide, especially chloride, and an acid of the formula

(10) $Y'-(CH_2)_{q-1}-Q'-(CH_2)_{p-1}-COOH$

or its ester, anhydride or halide especially chloride, are esterified or transesterified with an alcohol of formula:

(11) $HO-Xo_1-OH$

in which formulae Y, Y', Q, Q', *m*, *n*, *p* and *q*, are as hereinbefore defined, and Xo_1 denotes alkylene, alkenylene or alkynylene with 2 to 6 carbon atoms, which are optionally substituted by bromine or hydroxyl the radicals Q and Q' being substituted by bromine and/or having a double or triple bond; and bromine or hydrogen bromide is added on at any double bonds or triple bonds which are present in Q, Q' and Xo_1.

Specifically, in order to manufacture the aliphatic brominated monoesters of the formula (4), preferably an acid of the formula

(12) $H-(CH_2)_{m''-1}-Q_1-(CH_2)_{n''-1}-COOH$

or its anhydride or chloride, is esterified with a monoalcohol of the formula

(13) $HO-(CH_2)_{p''-1}-Q_1'-(CH_2)_{q''-1}-H$

in which formulae *m″*, *n″*, *p″* and *q″* are as hereinbefore defined and each of Q_1 and Q_1' independently denotes alkylene, alkenylene or alkynylene with 2 to 4 carbon atoms, which are optionally substituted by 2 to 4 bromine atoms, the radicals Q_1 and Q_1' being substituted by bromine and/or having a double or triple bond; and bromine or hydrogen bromide is added on to any double or triple bonds which are present.

The esterification is suitably carried out at 60 to 150°C in the melt or, preferably, in an optionally halogenated, cyclo-aliphatic, heterocyclic or aromatic hydrocarbon, as an inert solvent, and optionally in the presence of a strong acid as catalyst, and optionally in the presence of an optionally etherified hydroquinone as polymerisation inhibitor.

Suitable solvents are, for example, cyclohexane, 1,4-dioxane and, above all, toluene, benzene, chlorobenzene, *o*–, *m*– or *p*–xylene or a mixture thereof or mixtures of xylene/toluene or xylene/benzene. Benzene and toluene have proved to be the most suitable.

However, the esterification can also be carried out in the absence of solvents, that is to say in the melt.

The reaction is generally carried out at 60 to 150°C, or preferably at the boiling point of the solvents which are optionally also present, that is to say at 80 to 140°C, and especially 80 to 110°C, and the water which is formed during the reaction is removed from the reaction mixture as an azeotrope. At the temperature indicated, the reaction has generally ended after 12 to 24 hours.

Examples of possible acid catalysts, which are optionally employed in order to accelerate the esterification reaction, are inorganic acids, for example, hydrochloric acid, sulphuric acid or phosphoric acid, hydrogen bromide or organic sulphonic acids, for example *p*–toluenesulphonic acid. The acids which can be used are, in particular, anhydrous acids, preferably hydrogen chloride gas, hydrogen bromide or sulphuric acid monohydrate. It can be appropriate to add 4 to 5 g of the acid per mol of the component of the formula (7).

In order to prevent polymerisation of the ester obtained during the esterification reaction, this reaction is appropriately carried out in an inert nitrogen atmosphere. A polymerisation inhibitor can optionally be additionally employed. Examples of such inhibitors which may be mentioned are benzthiazine or, preferably, hydroquinone and especially an etherified hydroquinone, for example, hydroquinone monomethyl ether. Compared with hydroquinone, hydroquinone ethers have the advantage that they are able to prevent darkening of the esters. It can be appropriate to add 4 to 5 g of inhibitor per mol of the component of the formula (7).

The addition reaction with bromine or hydrogen bromide which is optionally to be carried out, is suitable effected at 10 to 60°C in the melt, or, preferably, in an optionally halogenated, aliphatic, cycloaliphatic, heterocyclic or aromatic hydrocarbon or in an aliphatic or cycloaliphatic ether as inert solvent,

and optionally in the presence of a bromide salt as catalyst.

This addition reaction essentially takes place when, in the formulae (7), (8), (9) and/or (10), Q and/or Q' denote alkenylene or alkynylene which are unsubstituted by bromine and when in the formula (11), Xo_1 denotes, alkynylene unsubstituted by bromine. Bromine or hydrogen bromide can be added on, both to unsaturated radicals Q and Q' of the acids of formulae (7), (9) and (10), or of their derivatives, and to unsaturated radicals Q' and Xo_1 of the alcohols of formulae (8) and (11) before the esterification reaction is carried out. Preferably, however, bromine or hydrogen bromide is added on, after the esterification reaction has taken place.

Suitable inert solvents for carrying out the addition reaction are, for example, cyclohexane, tetrahydrofuran, toluene, benzene, chlorobenzene and, above all, n-hexane and especially carbon tetrachloride. Examples of solvents which have proved most suitable are ethylene glycol monomethyl ether, dimethyl ether and trimethyl ether and, in particular, 1,4-dioxane.

However, the addition reaction can also be carried out in the absence of solvents, that is to say in the melt.

Alkaline earth metal salts, and above all alkali metal salts, of hydrogen bromide, for example, sodium bromide, and in particular ammonium bromide, may be mentioned as suitable bromide salts which are optionally employed as a catalyst for the addition reaction. It can be appropriate to add 2 to 4 g of a bromide salt per mol of the unsaturated compound which is subjected to the addition reaction with bromine or hydrogen bromide.

Generally the solvent and, optionally, the catalyst are initially introduced and then first bromine and subsequently the unsaturated compound, which is subjected to the addition reaction with bromine, are added at 10 to 60°C, and preferably 10 to 20°C, in the course of 3 to 6 hours. However, it is also possible initially to introduce the solvent, optionally the catalyst, and the unsaturated compound, which is subjected to the addition reaction with hydrogen bromide, and subsequently to pass in hydrogen bromide at 10 to 60°C, and preferably 10 to 20°C, in the course of 3 to 6 hours.

The reaction can be carried out in a particularly gentle manner by suspending dibromodioxane in 1,4-dioxane, 300 to 500 g of 1,4-dioxane being employed per mol of dibromodioxane, then adding the unsaturated compound to the suspension at 40 to 60°C in the course of 30 to 60 minutes and carrying the reaction to completion at 40 to 60°C in the course of 1 to 3 hours.

The bromine compounds of the present invention are suitable for use in spooling oils and cone oils which, for example, in the textile industry ensure that the necessary lubrication from fibre to fibre and from fibre to metal is provided during the processing of yarn. Furthermore, the bromine compounds according to the invention exhibit antistatic properties which, for example, are also of interest in the textile industry. However, a particularly important application of the bromine compounds according to the invention is their use as flameproofing agents.

The bromine compounds of the present invention can also be employed successfully for flameproofing organic synthetic fibre materials, the bromine compounds being incorporated into the spinning melt of the fibre materials, for example, into polyester spinning melts.

Preferably, however, the bromine compounds of the present invention are employed in the textile industry for flameproofing organic fibre materials.

Accordingly, a further subject of the present invention is a process for flameproofing organic, synthetic fibre materials, wherein a formulation, which is aqueous or present as an organic solution and which contains at least one bromine compound of the present invention and optionally at least one dispersing agent or emulsifier and/or a protective colloid, is applied to the fibre materials and the fibre materials are then dried and optionally subjected to a heat treatment.

Depending on whether the compound of the present invention is liquid or solid, it is possible for the aqueous formulations employed in the process optionally to contain dispersing agents or emulsifiers.

If the compound of the present invention is solid, it can, furthermore, optionally be so ground as an aqueous dispersion in the presence of a dispersing agent that the particles have an average diameter of 1 to 30μ. Good results are obtained, above all, with dispersions in which the particle size is 1 to 10 μ, especially 1 to 5 μ. The particle size in itself has no influence on the flameproofing effects which can be achieved but does have an influence on the stability of the dispersions.

If it is solid, the bromine compound of the present invention can optionally be ground in customary apparatuses suitable for such purposes, for example in a glass ball mill, a sand mill or in a corundum disc mill. Substances which can be used as components which are optionally added to the aqueous formulation are, for example, dispersing agents or emulsifiers customarily used in the dyestuffs and textile industries. The same applies in the case of the dispersing agents which are used if the compound

of the present invention is ground. Examples which may be mentioned are: lignin-sulphonates, aromatic sulphonic acids, saturated aliphatic dicarboxylic acids substituted by relatively long alkyl radicals, condensation products of aromatic sulphonic acids and formaldehyde, alkylphenol/ethylene oxide adducts, fatty acid/ethylene oxide adducts, fatty amines/ethylene oxide adducts or fatty alcohol/ethylene oxide adducts, sulphated, substituted benzimidazoles and sulphonated fatty acid amides. Good results are obtained, above all, with lignin-sulphonates, with substituted benzimidazoles or with condensation products of aromatic sulphonic acids and formaldehyde and especially with ethylene oxide adducts of alkylphenols, fatty amines, fatty alcohols or fatty acids.

Preferably, the dispersing agents used are those which, at elevated temperatures, for example at 180 to 220°C, do not lead to yellowing of the treated substrate or at most lead only to yellowing which can be removed on subsequent washing. In other words, the dispersing agents either should not decompose at elevated temperature or should form only soluble volatile decomposition products. The amount of dispersing agent employed is preferably from above 0 to 60 per cent by weight, relative to the bromine compound of the present invention. Particularly good results are achieved with 0 to 20, and especially 0 to 4, per cent by weight of dispersing agent, relative to the bromine compound of the present invention.

In order to improve the storage stability, the aqueous dispersions can also contain a protective colloid. Suitable protective colloids are those customarily used industrially, for example, polyvinyl alcohol, polyvinylpyrrolidone, methylcellulose, carboxymethylcellulose, hydroxyethylcellulose or hydroxypropylcellulose, gelatine, acid casein, starch paste or polymers of monomers of the acrylic acid series, such as polyacrylic acid or ethyl acrylate or methyl methacrylate copolymers. Good results are achieved, above all, with polyvinyl alcohol and hydroxyethylcellulose and especially with carboxymethylcellulose.

The aqueous formulations generally contain, per kg, 50 to 700 g, preferably 200 to 700 g, especially 200 to 500 g of the bromine compound of the present invention; 0 to 300 g, preferably 0 to 200 g, especially 0 to 40 g of the dispersing agent or emulsifier and 0 to 30 g, preferably 0 to 10 g, of the protective colloid. In each case the formulation is made up to 1 kg with water.

The formulations employed in the process for flameproofing organic fibre materials can not only be in the preferred aqueous form but also in the form of organic solutions. Such solutions contain neither dispersing agents nor emulsifiers nor protective colloids.

Examples of solvents which can be used are aliphatic alcohols, ketones or esters with at most 4 carbon atoms, for example, ethanol, acetone or ethyl acetate, or aromatic or cycloaliphatic hydrocarbons, for example, benzene or cyclohexane, or chlorinated, aliphatic hydrocarbons with 1 to 7 carbon atoms, for example, trichloroethylene, or mixtures thereof, for example, ethanol:methyl ethyl ketone in a ratio of 1 : 1.

In addition, by virtue of its advantageous solvent power for the compounds of the formula (1), dimethylformamide is of particular importance as a solvent.

Generally, the organic solutions contain 100 to 500 g, preferably 125 to 300 g and especially 150 to 250 g of the bromine compound of the present invention per kg of solution.

In the process according to the invention, the the formulations, which contain at least one bromine compound of the present invention, are applied to the organic, synthetic fibre materials by customary methods, for example by rinsing or printing and preferably by the exhaustion process or especially by padding.

In the case of the exhaustion process in particular, buffer substances, for example, sodium bicarbonate, disodium phosphate and trisodium phosphate or triethanolamine, preferably sodium acetate and especially ammonium acetate can optionally be added to the formulations in order to protect the organic, synthetic fibre materials to be provided with a flameproof finish.

After the formulations have been applied to the organic, synthetic fibre materials, the latter are dried and optionally subsequently subjected to a heat treatment at elevated temperature. A suitable method consists in drying the treated material at temperatures of up to 100°C, for example 70° to 100°C, and subjecting it to a heat treatment above 100°C, for example at up to 220°C, preferably at 120° to 220°C or, in particular, at 150° to 220°C, that is to say subjecting it to a thermosol process.

The thermosol process is preferably carried out at 175 to 220°C and generally lasts for 10 to 200 seconds and preferably 20 to 100 seconds. Particularly good results are obtained with times of 10 to 60 seconds.

The procedure according to the invention is preferably such that, depending on the nature of the fibre material and its weight per unit area, the coating of the bromine compound of the present invention, after the thermosol treatment, is 0.5 to 19, and preferably 1 to 12, per cent by weight, relative to the treated fibre material, this being achieved by suitable dilution of the aqueous or organic formulation with water or with the corresponding solvent.

Subsequent washing with an acid-binding agent, for example, sodium carbonate or sodium bicarbonate, can be advantageous.

Particularly preferred organic synthetic fibre

materials which are flameproofed according to the invention contain, for example, polyacrylonitrile fibres or preferably polyamide fibres and especially polyester fibres. Fibres made of acrylonitrile copolymers can also be flameproofed. The fibre materials can be in any stage of processing, that is to say they can be flameproofed as staple fibres or continuous filaments, as woven fabrics or knitted fabrics, when dyed or undyed, after treatment with optical brighteners or without such treatment or as textiles which have already been further processed. Preferably, however, the fibre material is a textile fibre material.

Polyamide fibres which can be used are, for example, those of poly-2-caprolactam, polyhexylmethylenediamine adipate or poly-ω-aminoundecanoic acid.

Preferably, however, it is polyester fibre materials which are finished. These materials are preferably those derived from terephthalic acid, for example poly-(ethylene glycol terephthalate) or poly-(1, 4-cyclohexylenedimethylene terephthalate). Examples of polyester fibres which can be effectively finished according to the invention are described in U.S.A. Patent Specifications 2,465,319 or 2,901, 446.

Mixtures of the synthetic fibres mentioned, for example polyacrylonitrile/polyester or polyamide/polyester, can also be flameproofed according to the invention.

According to the invention, permanent flameproofing effects, which are retained even after several washes or dry cleaning processes, are obtained on polyacrylonitrile fibre materials or polyamide fibre materials and especially on polyester fibre materials. The finishes furthermore have the advantage that the handle of the finished fibre materials is not felt to be oily, as is frequently the case when the known agents are used. The fastness to light and fastness to rubbings of dyeings is hardly affected. The whiteness of fabrics treated with optical brighteners is also barely affected even after a prolonged exposure, of, for example, 60 hours, to a FDA-RC type "Fadeometer" (Registered Trade Mark).

However, a particular advantage of the process according to the invention is based on the fact that, compared with known processes, better flameproofing effects are achieved with the application of smaller amounts.

Moreover, the textile-mechanical properties of the treated fibre materials are not adversely affected by the present flameproofing. By virtue of the fact that the amount is small, the good handle characteristics, in particular, of the treated fabrics are barely impaired. This is also true of the low flexural stiffness and the high tensile strength of the finished fibre materials. Printed fabrics can also be treated according to the invention without this resulting in a substantial impairment in the quality of the print.

The present flameproofing agents can also be employed at the same time as dyestuffs or optical brighteners, so that it is possible to dye or brighten and flameproof in a single process.

Good results are achieved even without a dispersing agent or emulsifier and when small amounts, for example 0.1 to 3 per cent by weight, relative to the liquor, of dispersing agent or emulsifiers are used, so that subsequent washing can optionally be dispensed with.

The following Examples serve to illustrate the present invention. Unless otherwise stated, the parts and percentages in the Examples are by weight.

EXAMPLE 1

Stage a). A solution of 145 parts (2.5 mols) of allyl alcohol in 500 parts by volume of benzene is added in the course of 80 minutes to a solution of 506.25 parts (2.5 mols) of 10-undecenoyl chloride and 3 parts of hydroquinone monomethyl ether in 1,250 parts by volume of anhydrous benzene.

The reaction mixture is heated to the reflux temperature and kept at this temperature for 23 hours. After distilling off the solvent, 523.6 parts (93.5% of theory) of the crude ester are obtained and this is subsequently distilled under 0.2 to 0.5 bars and at 80 to 100°C.

505 parts (90.2% of theory) of the distilled ester, which corresponds to the formula

(101) $CH_2=CH-(CH_2)_8-COO-CH_2-CH=CH_2$

are obtained as a colourless oil.

Elementary analysis gives the following values:

calculated; C : 74.9% H : 10.77% O : 14.25%
found: C : 74.7% H : 10.7% O : 14.6%

Stage b) 505 parts (2.03 mols) of dibromodioxane are suspended in 800 parts by volume of anhydrous 1, 4-dioxane. The suspension is heated to 50°C and 100 parts (0.848 mol) of the ester of the formula (101) are then added in the course of 30 minutes, whereupon the temperature of the reaction mixture rises to 60°C. After the reaction mixture has been cooled to 50°C, it is kept at 50°C for a further 2 hours. After distilling off the solvent, 440 parts (94.4% of theory) of the crude bromine compound are obtained and this is washed once with an aqueous, 10% strength sodium bisulphite solution and then with an aqueous 10% strength sodium chloride solution until neutral.

423 parts (92% of theory) of the purified bromine compound, which corresponds to the formula (6.1), are obtained as a yellow oil.

Elementary analysis gives the following values:

calculated: C : 30.91% H : 4.45% O : 5.88% Br : 58.76%
found: C : 31.2% H : 4.6% O : 6.2% Br : 58.0%

EXAMPLE 2

Stage a) 2 parts of hydrogen chloride gas are passed, in the course of 15 minutes, into a solution of 141.25 parts (0.5 mol) of oleic acid, 464 parts (8 mols) of allyl alcohol and 2 parts of hydroquinone monomethyl ether in 900 parts by volyme of anhydrous toluene. The reaction mixture is then heated to the reflux temperature and kept at this temperature for 24 hours.

After distilling off the solvent, 160 parts (~ 100% of theory) of the crude ester are obtained and this is then distilled under 0.1 to 0.08 bars and at 140 to 145°C.

145.4 parts (90.3% of theory) of the distilled ester, which corresponds to the formula

(102) $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COO-CH_2-CH=CH_2$

are obtained as a colourless oil.

Elementary analysis gives the following values:
calculated: C : 78.20% H : 11.88% O : 9.92%
found: C : 77.8% H : 11.0% O : 11.2%

Stage b) 140 parts (0.435 mol) of the ester of the formula (102) are brominated, in the manner described in stage b) of Example 1. with 254 parts (1.02 mols) of dibromodioxane in 400 parts by volume of 1, 4-dioxane. After distilling off the solvent, 280 parts (~ 100% of theory) of the crude bromine compound are obtained and this is washed as described in stage b) of Example 1.

274.8 parts (98.6% of theory) of the purified bromine compound, which corresponds to the formula (6.2), are obtained as a yellow oil. Elementary analysis gives the following values:
calculated: C : 39.50% H : 5.96% O : 4.98% Br : 49.75%
found: C : 39.4% H : 5.9% O : 6.6% Br : 48.1%

EXAMPLE 3

Stage a) A suspension of 112 parts (1 mol) of sorbic acid in 1,000 parts by volume of anhydrous cyclohexane is cooled to 20°C and 320 parts (2 mols) of bromine are added in the course of 2½ hours, the reaction mixture being kept at 20 to 30°C during the addition. The reaction mixture is then heated to 60°C and kept at this temperature for 2 hours. After the reaction mixture has cooled, the crystals which have separated out are filtered off.

406 parts (94.5% of theory) of crude 2,3,4,5-tetrabromocaproic acid are obtained as the material on the filter. The material on the filter is rinsed with anhydrous cyclohexane and 400 parts (93% of theory) of purified 2,3,4,5-tetrabromocaproic acid are then obtained.

Elementary analysis gives the following values:
calculated: C : 16.65% H : 1.87% O : 7.40% Br : 74.08%
found: C : 16.7% H : 1.9% O : 7.1% Br : 74.3%

Stage b) A solution of 34 parts (0.2 mol) of 10-undecen-1-ol in 100 parts by volume of anhydrous benzene is added in the course of 10 minutes, at 50°C, to a solution of 86.4 parts (0.2 mol) of tetrabromocaproic acid, 5 parts of sulphuric acid monohydrate and 0.2 part of hydroquinone monomethyl ether in 300 parts by volume of anhydrous toluene. The reaction mixture is then heated to the reflux temperature and kept at this temperature for 6 hours. After distilling off the solvent, 126.3 parts (108% of theory) of the ester are obtained as a brown oil, which cannot be distilled and which corresponds to the formula

(104) $CH_3-(CHBr)_4-COO-(CH_2)_9-CH=CH_2$

Elementary analysis gives the following values:
calculated: C : 34.95% H : 4.83% O : 5.47% Br : 54.70%
found: C : 35.5% H : 5.0% O : 7.0% Br : 53.0%

Stage c) A suspension of 15 parts of ammonium bromide in 300 parts by volume of anhydrous 1, 4-dioxane is cooled to 10°C and, in the course of 4 hours, 38 parts (0.24 mol) of bromine and then 126 parts (0.22 mol) of the ester of the formula (104) are added, the reaction mixture being kept at 10 to 20°C during these additions.

The crude bromine compound is then filtered off from the reaction mixture and dissolved in diethyl ether. The etherial solution is washed with an aqueous 2% strength sodium carbonate solution until neutral and dried over sodium sulphate.

After removing the diethyl ether 72.3 parts (45.0%) of theory) of the purified bromine compound, which corresponds to the formula (6.3), are obtained as a yellow, viscous oil.

Elementary analysis gives the following values:
calculated: C : 27.41% H : 3.80% O : 4.30% Br : 64.50%
found: C : 28.0% H : 3.9% O : 6.1% Br : 62.0%

EXAMPLE 4

Stage a) 5 parts of hydrogen bromide are passed, in the course of 10 minutes, into a solution of 86 parts (1 mol) of crotonic acid, 170 parts of 10-undecen-1-ol and 2 parts of hydroquinone monomethyl ether in 800 parts by volume of anhydrous toluene. The reaction mixture is then heated to the reflux temperature and kept at this temperature for 6 hours.

After distilling off the solvent, 253 parts (106% of theory) of the crude ester are obtained and this is then distilled under 0.15 bars and at 120 to 146°C.

211.2 parts (88.7% of theory) of the distilled ester, which corresponds to the formula

(106) $CH_3-CH=CH-COO-(CH_2)_9-CH=CH_2$

are obtained as a clear, pale yellow oil.

Elementary analysis gives the following values:

calculated: C : 75.40% H : 11.00% 0 : 13.4%
found: C : 74.9% H : 11.5% 0 : 13.6%

Stage b) 211.2 parts (0.88 mol) of the ester of the formula (106) are brominated, in the manner described in stage b) of Example 1, with 340 parts (2.125 mols) of bromine in 1,100 parts by volume of 1, 4-dioxane. After distilling off the solvent, 480 parts (93.4% of theory) of the crude bromine compound are obtained and this is washed as described in stage b) of Example 1.

414 parts (80.5% of theory) of the purified bromine compound, which corresponds to the formula (6.4), are obtained as a yellow oil.

Elementary analysis gives the following values:

calculated: C : 32.29% H : 4.69% 0 : 5.73% Br : 57.28%
found: C : 33.2% H : 5.6% 0 : 6.1% Br : 55.1%

EXAMPLE 5

Stage a) 5 parts of hydrogen bromide are passed, in the course of 10 minutes, into a solution of 86 parts (1 mol) of crotonic acid, 268 parts (1 mol) of oleyl alcohol and 2 parts of hydroquinone monomethyl ether in 1,000 parts by volume of anhydrous toluene. The reaction mixture is then heated to the reflux temperature and kept at this temperature for 6 hours. After distilling off the solvent, 384.2 parts (114% of theory) of the crude ester are obtained and this is subsequently distilled under 0.08 bar and at 176 to 181°C. 294 parts (88.6% of theory) of the distilled ester, which corresponds to the formula

(107) $CH_3-CH=CH-COO-(CH_2)_8-CH=CH-(CH_2)_7-CH_3$

are obtained as a colourless oil.

Elementary analysis gives the following values:

calculated: C : 78.45% H : 11.95% 0 : 9.51%
found: C : 78.6% H : 12.7% 0 : 8.7%

Stage b) 272 parts (0.81 mol) of the ester of the formula (107) are brominated, in the manner described in stage b) of Example 1, with 310 parts (1.94 mols) of bromine in 1,200 parts by volume of 1, 4-dioxane. After distilling off the solvent, 500 parts (94% of theory) of the crude bromine compound are obtained and this is washed in the manner described in stage b) of Example 1.

485 parts (91.3% of theory) of the purified bromine compound, which corresponds to the formula (6.5), are obtained as a yellow oil.

Elementary analysis gives the following values:

calculated: C : 40.2% H : 6.14% 0 : 4.87% Br : 48.70%
found: C : 41.6% H : 7.0% 0 : 5.4% Br 46.0%

EXAMPLE 6

Stage a) A solution of 86 parts (1 mol) of 2-butyne-1, 4-diol, 405 parts (2 mols) of 10-undecenoyl chloride and 2 parts of hydroquinone monomethyl ether in 1,500 parts by volume of anhydrous toluene is heated to the reflux temperature and kept at this temperature for 13 hours. After distilling off the solvent, 425.5 parts (102% of theory) of the crude ester are obtained and this is subsequently distilled under 0.5 bar and at 128 to 163°C. 362 parts (86.5% of theory) of the distilled ester, which corresponds to the formula

(108) $CH_2=CH-(CH_2)_8-COO-CH_2-C\equiv C-CH_2-OOC-(CH_2)_8-CH=CH_2$

are obtained as a clear, pale yellow oil.

Elementary analysis gives the following values:

calculated: C : 75.40% H : 11.00% 0 : 13.42%
found: C . 74.9% H : 11.5% 0 : 13.6%

Stage b) 209 parts (0.5 mol) of the ester of the formula (108) are brominated, in the manner described in stage b) of Example 1, with 372 parts (1.5 mols) of dibromodioxane in 1,200 parts by volume of 1, 4-dioxane. After distilling off the solvent, 420 parts (93.5%) of theory) of the crude bromine compound are obtained and this is washed in the manner described in stage b) of Example 1.

394 parts (87.8% of theory) of the purified bromine compound, which corresponds to the formula (6.6) are obtained as a yellow oil.

Elementary analysis gives the following values:

calculated: C : 34.80% H : 4.71% 0 : 7.13% Br : 53.40%
found: C : 35.6% H : 4.9% 0 : 8.2% Br : 51.3%

EXAMPLE 7

Stage a) A solution of 44 parts (0.5 mol) of 2-butene-1, 4-diol, 202.5 parts (1 mol) of 10-undecenoyl chloride and 2 parts of hydroquinone monomethyl ether in 800 parts by volume of anhydrous toluene is heated to the reflux temperature and kept at this temperature for 12 hours. After distilling off the solvent, 207.8 parts (99% of theory) of the crude ester are obtained and this is subsequently distilled under 0.07 bar and at 180 to 190°C. 189.9 parts (90.5% of theory) of the distilled ester, which corresponds to the formula

(109) $CH_2=CH-(CH_2)_8-COO-CH_2-CH=$

$CH-CH_2-OOC-(CH_2)_8-CH=CH_2$

are obtained as a colourless oil.

Elementary analysis gives the following values:
calculated: C : 74.24% H : 10.54% O : 15.22%
found: C : 73.9% H : 10.5% O : 15.6%

Stage b) 240 parts (1.5 mols) of bromine are added in the course of one hour to a suspension of 1 part of ammonium bromide in 1,000 parts by volume of anhydrous 1,4-dioxane and subsequently a solution of 209 parts (0.5 mol) of the ester of the formula (108) in 300 parts by volume of anhydrous, 1,4-dioxane is added, at 10 to 20°C, in the course of 30 minutes. The reaction mixture is kept at 10 to 20°C for 16 hours. After removing the solvent *in vacuo* at 20°C, 420 parts (93.5% of theory) of the crude bromine compound are obtained and this is washed in the manner described in stage b) of Example 1. 186.3 parts (85.6% of theory) of the purified bromine compound, which corresponds to the formula (6.7), are obtained as a yellow oil.

Elementary analysis gives the following values:
calculated: C : 34.70% H : 4.92% O : 7.12% Br : 53.25%
found: C : 34.3% H : 5.0% O : 8.0% Br : 52.7%

EXAMPLE 8

Stage a) The procedure is as described in stage a) of Example 7 but no hydroquinone monomethyl ether is added. After distilling off the solvent, 207.8 parts (99% of theory) of the crude ester are obtained and this is subsequently subjected to a vacuum distillation.

In this batch, 78.1 parts (37.3% of theory) of a distilled ester which corresponds to the formula

(aa0) $CH_2=CH-(CH_2)_8-COO-CH_2-CH=CH-CH_2-OH$

are obtained, as a pale yellow oil, as the first fraction, which distils under 0.1 to 0.07 bar and at 98 to 131°C, and 99 parts (47.1% of theory) of a distilled ester which corresponds to the formula

(111) $CH_2=CH-(CH_2)_8-COO-CH_2-CH=CH-CH_2-OOC-(CH_2)_8-CH=CH_2$

are obtained, as a colourless oil, as the second fraction, which distils under 0.07 bar and at 178 to 195°C.

Elementary analysis of the ester of the formula (110) gives the following values:
calculated: C : 70.8% H : 10.3% O : 18.9%
found: C : 69.5% H : 10.2% O : 20.3%

Elementary analysis of the ester of the formula (111) gives the following values:
calculated: C : 74.24% H : 10.54% O : 15.21%
found: C : 73.5% H : 10.5% O : 16.0%

Stage b) In the manner described in stage b) of Example 7, 70 parts (0.275 mol) of the ester of the formula (110) are brominated, in the presence of ammonium bromide, with 105.8 parts (0.552 mol) of bromine in anhydrous 1,4-dioxane.

157.5 parts (99.5% of theory) of the crude bromine compound are obtained and this is washed in the manner described in stage b) of Example 1.

145.1 parts (91.9% of theory) of the purified bromine compound, which corresponds to the formula (6.8) are obtained as a yellow, clear viscous oil.

Elementary analysis gives the following values:
calculated: C : 31.40% H : 4.57% O : 8.37% Br : 55.80%
found: C : 33.0% H : 4.9% O : 9.1% Br : 53.0%

Stage c) 105 parts (0.25 mol) of the ester of the formula (111) are brominated, in the manner described in stage b) of Example 7, with 144 parts (0.9 mol) of bromine in anhydrous 1,4-dioxane. The crude bromine compound is purified in the manner described in stage b) of Example 1.

186.3 parts (82.72% of theory) of the purified bromine compound, which corresponds to the formula (6.7), are obtained as a yellow, clear, viscous oil.

Elementary analysis gives the following values:
calculated: C : 34.70% H : 4.92% O : 7.12% Br : 53.25%
found: C : 34.3% H : 5.02% O : 8.2% Br : 52.5%

EXAMPLE 9

The procedure is as indicated in stage b) of Example 3 but 0.5 mol of tetrabromocaproic acid is employed in place of 0.2 mol and 0.25 mol of ethylene glycol is employed in place of 0.2 mol of 10-undecen-1-ol.

After the reaction mixture has been warmed to the boil under reflux for 6 hours, the product is filtered off. The residue is rinsed with anhydrous cyclohexane, whereupon 54 g (24.2% of theory) of the purified ester of the formula (6.9), are obtained as white crystals which have a melting point of 197 to 205°C.

Elementary analysis gives the following values:
calculated: C : 18.90% H : 2.04% O : 7.19% Br : 71.86%
found: C : 17.6% H : 1.8% O : 12.8% Br : 68.8%

The filtrate contains 150 parts (70% of the amount employed) of unreacted tetrabromocaproic acid which can be used again.

EXAMPLE 10

Stage a) A solution of 405 parts (2 mols) of 10-undecenoyl chloride, 62 parts (1 mol) of ethylene glycol and 1 part of hydroquinone monomethyl ether in 800 parts by volume of anhydrous toluene is heated to the reflux temperature and kept at this temperature for 6 hours. After distilling off the solvent, 388 parts (98.6% of theory) of the crude ester are obtained and this is subsequently distilled under 0.1 bar and at 140 to 182°C. 381.2 parts (98.3% of theory) of the distilled ester, which corresponds to the formula

(113) $CH_2{=}CH{-}(CH_2)_8{-}COO{-}(CH_2)_2{-}OOC{-}(CH_2)_8{-}CH{=}CH_2$

are obtained as a pale yellow oil.

Elementary analysis gives the following values:

calculated: C : 73.05% H : 10.72% O : 16.23%
found: C : 72.7% H : 10.7% O : 16.6%

Stage b) In the manner described in stage b) of Example 7, 198 parts (0.5 mol) of the ester of the formula (113) are brominated, in the presence of ammonium bromide, with 176 parts (1.1 mols) of bromine in anhydrous 1, 4-dioxane.

367.6 parts (102.5% of theory) of the crude bromine compound are obtained and this is washed in the manner described in stage b) of Example 1.

362.5 parts (101% of theory) of the purified bromine compound, which corresponds to the formula (6.10), are obtained as a pale yellow oil.

Elementary analysis gives the following values:

calculated: C : 40.35% H : 5.93% O : 8.97% Br : 44.80%
found: C : 40.6% H : 5.9% O : 9.2% Br : 44.3%

EXAMPLE 11

Polyester fabrics with a weight per unit area of 162 g/m² are padded with the aqueous liquors according to Table 1 which follows, dried at 80°C for 30 minutes and then thermosol-treated at 200°C for 20 seconds. The liquor pick-up is 65%.

The fabric is then washed, after treatment, for 5 minutes at 60°C in a liquor which contains, per litre, 4 g of anhydrous sodium carbonate and 1 g of a condensation product of 1 mol of *p*-nonylphenol and 9 mols of ethylene oxide. It is then rinsed and dried.

The handle characteristics of the individual fabrics are then tested.

The handle is tested by hand and given handle ratings in accordance with the following scale:

0 unchanged
1 marginally stiffer than 0
2 somewhat stiffer than 0
3 stiff
4 very stiff

The fabrics are then washed 20 times and 40 times for 45 minutes at 60°C, in a domestic washing machine, in a liquor which contains 4 g/l of a household detergent (SNV 198,861-wash).

The flameproof character of the individual samples of fabric is then tested (vertical test DIN 53,906, ignition time 3 seconds).

The results are summarised in Table 1, which follows.

Similar results are obtained with the bromine compounds according to Examples 2 to 8 and 10.

TABLE 1

Treatment	Treated fabric	Untreated fabric
Liquor No.		
Composition of the liquor in g/1		
Bromine compound according to Example 1	154	–
Reaction product of 1 mol of coconut fatty acid and 2 mols of diethanolamine (90%)	85	–
Coating in %		
after drying	6.4	–
after the thermosol treatment	5.6	–
Flameproof character		
BT = burning time in seconds		
TL = tear length in cm		
after 20 machine washes BT	0	burns
TL	7.5	
after 40 machine washes BT	2	burns
TL	7.5	
handle rating	1	0

TABLE 2

Treatment	Treated fabric					Untreated fabric
Liquor No.	1	2	3	4	5	
Composition of the liquor in g/1						
Bromine compound according to Example 1	100	100	100	100	100	–
Sorbitol monooleate/ethylene oxide adduct (100%)	10	–	–	–	–	–
Hydroabietyl alcohol/ethylene oxide adduct, crosslinked with hexamethylene 1, 6-diisocyanate (100%)	–	5	10	20	–	–
Isooctyl-phenyl-polyethoxyethanol (100%)	–	–	–	–	10	–
Bromine content of the treated fabric in %						
after the thermosol treatment	2.50	2.56	2.31	2.32	3.38	0
after the post-treatment wash	2.05	2.06	1.86	1.82	2.45	0
after 20 washes	1.87	1.95	1.96	1.53	2.18	0
Flameproof character after 20 machine washes						
burning time in seconds	0	0	0	1	0	
tear length in cm	7.5	7.5	7.5	7	7.5	burns

EXAMPLE 12

Polyester fabrics with a weight per unit area of 162 g/m^2 are padded with the aqueous liquors according to Table 2 which follows, which contain the product according to Example 1 and various dispersing agents, dried for 30 minutes at 80°C and then thermosol-treated at 200°C for 30 seconds. The liquor pick-up is 60%.

The post-treatment wash, the 20 washes in the domestic washing machine and the testing of the flameproof character are carried out as indicated in Example 11.

The results are summarised in Table 2.

EXAMPLE 13

The procedure is as indicated in Example 12 but the thermosol treatment is carried out at 175°C and 40 washes are carried out in the domestic washing machine.

The results are summarised in Table 3 which follows.

TABLE 3

Treatment	Treated fabric		Untreated fabric
Liquor No.	1	2	
Composition of the liquor in g/l			
Bromine compound according to Example 1	100	100	–
Sorbitol monooleate/ethylene oxide adduct (100%)	10	–	–
Hydroabietyl alcohol/ethylene oxide adduct, crosslinked with hexamethylene 1, 6-diisocyanate (100%)	–	20	–
Bromine content of the treated fabric in %			
after the thermosol treatment	2.30	2.18	0
after the post-treatment wash	1.84	1.70	0
after 40 washes	1.27	1.30	0
Flameproof character after 40 machine washes			
burning time in seconds	3	0	
tear length in cm	7.5	7	burns

TABLE 4

Treatment	Treated fabric		Untreated fabric
Liquor No.	1	2	
Composition of the liquor in g/l			
Bromine compound according to Example 1	10	10	–
Sorbitol monooleate/ethylene oxide adduct (100%)	0.5	0.5	–
Ammonium acetate	10	10	–
Condensation product of naphthalenesulphonic acid and formaldehyde (100%)	5	10	–
Bromine content of the treated fabric in %			
after the exhaustion treatment	2.60	2.10	0
after 20 washes	1.62	1.70	0
Degree of exhaustion in %	49	40	–
Flameproof character BT = burning time in seconds TL = tear length in cm			
after exhaustion treatment BT	0	1	16
TL	8	6.5	10
after 20 washes BT	2	0	15
TL	8	7	11.5

TABLE 5

Treatment	Treated fabric				Untreated fabric
Liquor No.	1	2	3	4	
Composition of the liquor in g/l					
Bromine compound according to Example 1	4	8	12	16	–
Sorbitol monooleate/ethylene oxide adduct (100%)	0.2	0.4	0.6	0.8	–
Ammonium acetate	5	10	15	20	–
Bromine content of the treated fabric in %					
after the exhaustion treatment	1.18	2.25	3.88	3.88	0
after 40 washes	1.11	0.44	1.75	1.84	0
Degree of exhaustion in %	55	53	63	47	–
Flameproof character BT = burning time in seconds TL = tear length in cm					
aftr exhaustion treatment BT	4	2	0	0	16
TL	9	8.5	8	8.5	10
after 40 washes BT	2	0	0	1	14
TL	9	7.5	7.5	9	9

EXAMPLE 14

Using a liquor ratio of 1 : 10, polyester fabrics with a weight per unit area of 162 g/m^2 are treated, under a pressure of 5 atmospheres gauge, for 30 minutes at 130°C, by the exhaustion process, with the aqueous liquors according to Table 4 which contain the product according to Example 1.

In contrast to Example 11 in the present Example the fabrics are not given a post-treatment wash.

On the contrary, after the exhaustion treatment, the fabrics are washed 20 times for 45 minutes at 60°C, in a domestic washing machine, in a liquor which contains 4 g/l of a household detergent (SNV 198,861 wash).

The flameproof character of the individual samples of fabric is then tested (vertical test DIN 53,966, ignition time 3 seconds).

The results are summarised in Table 4.

EXAMPLE 15

The procedure is as indicated in Example 14 but 40 washes are carried out in the domestic washing machine.

The results are summarised in Table 5.

EXAMPLE 16

Polyester fabrics with a weight per unit area of 162 g/m^2 are padded with solutions, according to Table 6 which follows, of the bromine compounds according to the invention in dimethylformamide, dried for 30 minutes at 80°C and then thermosol-treated at 200°C for 20 seconds.

The fabric is then washed, after treatment, as indicated in Example 11 and its handle characteristics are tested and the fabric is washed up to 20 times in a domestic washing machine and its flameproof character is tested.

The results are summarised in Table 6 which follows.

Similar results are obtained with the bromine compounds according to Examples 1 and 10.

TABLE 6

Treatment	Treated fabric					Untreated fabric
Liquor No.	1	2	3	4	5	
Composition of the liquor in g/l						
Bromine compound according to Example 2	250	—	—	—	—	—
" " " " " 3	—	123	—	—	—	—
" " " " " 4	—	—	250	—	—	—
" " " " " 5	—	—	—	250	—	—
" " " " " 6	—	—	—	—	250	—
Liquor pick-up in %	60	65	60	60	60	—
Coating in %						
after drying	18.1	6.9	16.2	11.8	17.9	—
after the thermosol treatment	17.2	5.6	12.7	10.7	9.5	—
after the post-treatment wash	9	5.3	12.3	9.3	8.2	—

Table 6 (continuation)

Treatment	Treated fabric					Untreated fabric
Liquor No.	1	2	3	4	5	
Handle rating	1	0	1	1	1	0
Flameproof character BT = burning time in seconds TL = tear length in cm						
after thermosol treatment BT	0	2	0	0	0	burns
TL	7.5	8	7	8	7.5	
after post-treatment wash BT	3	2	2	2	0	burns
TL	8.5	7.5	8.5	8	0.5	
after 20 machine washes BT	3	3	4	—	2	burns
TL	7	8.5	8	—	7.5	
after 40 machine washes BT	—	0	4	—	0	burns
TL	—	7	7	—	7	

EXAMPLE 17

The procedure is as indicated in Example 14 but exhaustion liquors having the composition indicated in Table 8, which follows, are used and 20 washes and 40 washes are carried out according to SNV 198,861.

The results obtained when the flameproof character was tested in accordance with DIN 53,966 with an ignition time of 3 seconds are summarised in Table 8.

EXAMPLE 18

The procedure is as indicated in Example 16 but the polyester fabrics are padded in liquors having the composition indicated in Table 9, which follows.

The results are summarised in Table 9, which follows.

TABLE 8

Liquor specification	Treated fabric 1	2	3	4	Untreated fabric
Composition of the liquor					
Constituents in g/l					
Bromine compound according to Example 7 or to stage c) of Example 8	5	10	–	–	–
Bromine compound according to stage b) of Example 8	–	–	5	10	–
Reaction product of 1 mol of coconut fatty acid and 2 mols of diethanolamine (90%)	0.25	0.5	0.25	0.10	–
Bromine content of the treated fabric in % after the exhaustion treatment	0.5	1.57	0.3	0.4	0
Flameproof character					
after 20 washes BT	3	2	0	0	burns
TL	8	6.5	8	7.5	
after 40 washes BT	1	0	1	0	burns
TL	7.5	7.5	7.5	7.5	

TABLE 9

Liquor specification	Treated fabric 1	2	3	4	5	Untreated fabric
Composition of the liquor						
Constituents in g/l						
Bromine compound according to Example 7 or to stage c) of Example 8	125	250	–	–	–	–
Bromine compound according to stage b) of Example 8	–	–	125	250	–	–
Bromine compound according to Example 9	–	–	–	–	133	–
Liquor pick-ups in %	60	60	60	60	90	–
Coating in %						
after drying	9.2	15.1	7.9	15.8	8.9	–
after the thermosol treatment	8.8	14.7	6.10	13	6	–
after the post-treatment wash	7.6	10.1	5.3	11	2.8	–
Handle rating	½	½	1½	1¾	1¼	0
Flameproof character						
before the thermosol treatment BT	1	0	0	0	8	burns
TL	7.5	5.5	9	8	6.5	
after the thermosol treatment BT	2	1	2	0	8	burns
TL	7	7.5	7	7.5	8.5	
after the post-treatment wash BT	0	0	0	0	4	burns
TL	6.5	6.5	7.5	7	6	
after 20 machine washes BT	5	5	3	0	2	burns
TL	7.5	7	7.5	6.5	5	
after 40 machine washes BT	2	3	0	0	3	burns
TL	7	7.5	7.5	7	5	

WHAT WE CLAIM IS:–

1. A bromine compound of the general formula

$$Y-(CH_2)_{m-1}-(CHBr)_r-(CH_2)_{n-1}-COO-(X_1-OOC)_{t-1}-(CH_2)_{p-1}-(CHBr)_s-(CH_2)_{q-1}-Y'$$

containing up to 14 bromine atoms, in which X_1 denotes alkylene or alkenylene with 2 to 6 carbon atoms which are optionally substituted by bromine or hydroxyl, each of Y and Y' independently denotes hydroxyl or hydrogen, each of m, n, p and q independently denotes an integer from 1 to 13, at least two of m, n, p and q being at least 2, each of r and s independently denotes an integer from 1 to 7, t denotes 1 or 2, with the proviso that the sum of $m + n + r$ is an integer from 4 to 20, the sum of $p + s + q$ is an integer from 4 to 20, and the sum of $m + n + p + q + r + s$ is an integer from 13 to 40.

2. A bromine compound according to claim 1, of the formula

$$H-(CH_2)_{m-1}-(CHBr)_r-(CH_2)_{n-1}-COO-(X_1-OOC)_{t-1}-(CH_2)_{p-1}-(CHBr)_s-(CH_2)_{q-1}-H$$

in which X_1, m, n, p, q, r, s and t are as defined in claim 1.

3. A bromine compound according to claim 1 or 2, or the formula

$$H-(CH_2)_{m'-1}-(CHBr)_{r'}-(CH_2)_{n'-1}-COO-(X_2-OOC)_{t-1}-(CH_2)_{p'-1}-(CHBr)_{s'}-(CH_2)_{q'-1}-H$$

in which X_2 denotes alkylene with 2 to 4 carbon atoms which is optionally substituted by bromine or hydroxyl or denotes alkenylene with 2 to 4 carbon atoms which is optionally substituted by bromine, each of m', n', p' and q' independently is an integer from 1 to 10, two or three of m', n', p' and q' being an integer from 2 to 10, each of r' and s' independently is an integer from 2 to 4, t is 1 or 2, with the proviso that the sum of $m' + n' + r'$ is an integer from 4 to 20, the sum of $p' + s' + q'$ is an integer from 4 to 20, and the sum of $r' + s' + m' + n' + p' + q'$ is an integer from 13 to 40.

4. A bromine compound according to any one of the preceding claims, of the formuls

$$H-(CH_2)_{m''-1}-(CHBr)_{r'}-(CH_2)_{n''-1}-COO-(CH_2)_{p''-1}-(CHBr)_{s'}-(CH_2)_{q''-1}-H$$

in which each of m'', n'', p'' and q'' independently is an integer from 1 to 9, two of m'', n'', p'' and q'' being an integer from 2 to 9, each of r' and s' independently is an integer from 2 to 4, with the proviso that the sum of $m'' + n'' + r'$ is an integer from 4 to 20, the sum of $p'' + s' + q''$ is an integer from 4 to 20 and the sum of $r' + s' + m'' + n'' + p'' + q''$ is an integer from 13 to 40.

5. A bromine compound according to any one of the preceding claims wherein the sum of $r + s + m + n + p + q$ or $r' + s' + m' + n' + p' + q'$ or $r' + s' + m'' + n'' + p'' + q''$ is an integer from 13 to 24.

6. A bromine compound according to any one of the preceding claims, which has a molecular weight of 300 to 1,300.

7. A bromine compound according to claim 6, which has a molecular weight of 440 to 900.

8. A bromine compound according to any one of the preceding claims, wherein the bromine content is 30 to 80 percent by weight.

9. A bromine compound according to claim 8, wherein the bromine content is 40 to 65 per cent by weight.

10. A bromine compound according to claim 1 specifically identified herein.

11. A process for the manufacture of a bromine compound as claimed in claim 1, wherein either:

(A) an acid of the formula

$$Y-(CH_2)_{m-1}-Q-(CH_2)_{n-1}-COOH$$

or its ester, anhydride or halide is esterified or transesterified with an alcohol of the formula

$$HO-(CH_2)_{p-1}-Q'-(CH_2)_{q-1}-Y'$$

in which formulae, Y, Y', m, n, p and q are as defined in claim 1 and each of Q and Q' independently denotes alkylene, alkenylene or alkynylene with at most 7 carbon atoms, which are optionally substituted by 1 to 7 bromine atoms, the radicals Q and Q' being substituted by bromine and/or having a double or triple bond;
and bromine or hydrogen bromide is added on at any double bonds or triple bonds which are present; or

(B) an acid of the formula

$$Y-(CH_2)_{m-1}-Q-(CH_2)_{n-1}-COOH$$

or its ester, anhydride or halide, and an acid of the formula

$$Y'-(CH_2)_{q-1}-Q'-(CH_2)_{p-1}-COOH$$

or its ester, anhydride or halide are esterified or transesterified with an alcohol of formula

$$HO-Xo_1-OH$$

in which formulae Y, Y', m, n, p and q are as defined in claim 1 and Q and Q' are as defined above and Xo_1 denotes alkylene, alkenylene or alkynylene with 2 to 6 carbon atoms, which are optionally substituted by bromine or hydroxyl, the radicals Q and Q' being substituted by bromine and/or having a double or triple bond; and

bromine or hydrogen bromide is added on at any double or triple bonds which are present in Q, Q' and Xo_1.

12. A process according to claim 11 for the manufacture of a bromine compound as claimed in claim 4, wherein an acid of the formula:

$$H{-}(CH_2)_{m''-1}{-}Q_1{-}(CH_2)_{n''-1}{-}COOH$$

or its anhydride or chloride, is esterified with a monoalcohol of the formula

$$HO{-}(CH_2)_{p''-1}{-}Q_1'{-}(CH_2)_{q''-1}{-}H$$

in which formulae m'', n'', p'' and q'' are as defined in claim 4 and each of Q_1 and Q_1' independently denotes alkylene, alkenylene or alkynylene with 2 to 4 carbon atoms, which are optionally substituted by 2 to 4 bromine atoms, the radicals Q_1 and Q_1' being substituted by bromine and/or having a double or triple bond; and bromine or hydrogen bromide is added on to any double or triple bonds which are present.

13. A process according to claim 11 or 12, wherein the esterification is carried out at 60 to 150°C in the melt or in an optionally halogenated, cycloaliphatic, heterocyclic or aromatic hydrocarbon as inert solvent, and optionally in the presence of a strong acid as catalyst, and optionally in the presence of an optionally etherified hydroquinone as polymerisation inhibitor.

14. A process according to any one of claims 11 to 13 wherein the addition reaction with bromine or hydrogen bromide is carried out at 10 to 60°C in the melt or in an optionally halogenated, aliphatic, cycloaliphatic, heterocyclic or aromatic hydrocarbon or in an aliphatic or cycloaliphatic ether as inert solvent, and optionally in the presence of a bromide salt as catalyst.

15. A process according to claim 11, substantially as described in any one of Examples 1 to 8 and 10.

16. A process according to claim 11, substantially as described in Example 9.

17. A bromine compound according to any one of claims 1 to 9 whenever manufactured by a process as claimed in any one of claims 11 to 15.

18. A bromine compound according to claim 10 whenever manufactured by a process as claimed in claim 16.

19. A process for flameproofing an organic synthetic fibre material, wherein a formulation, which is aqueous or in the form of an organic solution and which contains at least one bromine compound as claimed in any one of claims 1 to 10, 17 and 18 is applied to the material and the material is then dried.

20. A process according to claim 19 wherein the formulation is aqueous and contains at least one dispersing agent or emulsifier.

21. A process according to claim 19 or 20, wherein the formulation is aqueous and contains at least one protective colloid.

22. A process according to claim 20 or 21, wherein the formulation is in the form of an aqueous dispersion or emulsion which contains, as the dispersing agent or emulsifier, an ethylene oxide adduct of an alkylphenol, fatty alcohol or fatty acid.

23. A process according to claim 20, 21 or 22, wherein the formulation is in the form of an aqueous dispersion which contains, as the protective colloid, polyvinyl alcohol, hydroxymethylcellulose or carboxymethylcellulose.

24. A process according to claim 19, wherein the formulation is in the form of an organic solution in an aliphatic alcohol, ketone or ester with at most 4 carbon atoms, in an aromatic or cycloaliphatic hydrocarbon or in a chlorinated, aliphatic hydrocarbon with 1 to 7 carbon atoms or in a mixture thereof.

25. A process according to claim 19, wherein the formulation is in the form of an organic solution in dimethylformamide.

26. A process according to any one of claims 19 to 25, wherein the formulation is applied to the material by the padding process.

27. A process according to any one of claims 19 to 25, wherein the formulation is applied to the material by the exhaustion process.

28. A process according to any one of claims 19 to 26, wherein the dried material is subjected to a heat treatment.

29. A process according to claim 28 wherein the heat treatment is carried out at 120° to 220°C.

30. A process according to claim 29 wherein the heat treatment is carried out at 150° to 220°C.

31. A process according to claim 19, wherein the bromine compound is as claimed in any one of claims 1 to 9 and 17.

32. A process according to claim 31 substantially as described in any one of Examples 11 to 15.

33. A process according to claim 19 substantially as described in Example 16, 17 or 18.

34. An organic synthetic fibre material whenever provided with a flameproof finish by a process as claimed in any one of claims 19 to 33.

35. A material according to claim 34 which comprises polyester, polyamide and/or polyacrylonitrile.

36. A material according to claim 34 or 35

whenever provided with a flameproof finish by a process as claimed in claim 31 or 32.

37. A flameproofing agent which contains at least one bromine compound as claimed in any one of claims 1 to 10, 17 and 18 and water or at least one solvent and, optionally, when water is present, at least one dispersing agent or emulsifier and/or a protective colloid.-

38. A flameproofing agent according to claim 37, wherein the bromine compound is as claimed in any one of claims 1 to 9 and 17.

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